

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C11D 3/39, 3/395, 3/20, 3/10, 17/04, 3/00, 11/00	A1	(11) International Publication Number: WO 98/33880 (43) International Publication Date: 6 August 1998 (06.08.98)
--	----	--

(21) International Application Number: PCT/US98/01744 (22) International Filing Date: 30 January 1998 (30.01.98) (30) Priority Data: 08/795,618 5 February 1997 (05.02.97) US (71) Applicant: S. C. JOHNSON & SON, INC. [US/US]; 1525 Howe Street, Racine, WI 53403 (US). (72) Inventors: SVOBODA, George, J.; 4973 North Lake Drive, Whitefish Bay, WI 53217 (US). GIPP, Mark, M.; 5912 Independence Road, Racine, WI 53406 (US). (74) Agents: BOZEK, Laura, L. et al.; S. C. Johnson & Son, Inc., Patent Section, 1525 Howe Street, Racine, WI 53403 (US).	(81) Designated States: AU, BR, CA, CN, JP, MX, NZ, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
---	---

(54) Title: BLEACHING CLEANER THAT FOAMS

(57) Abstract

Disclosed herein are binary form liquid cleaners that foam. In one form, one part contains a peroxide such as hydrogen peroxide and may contain a weak acid. The other part contains a carbonate, hypochlorite, hypochlorite generator, or manganese containing material. At least one of the two parts also contains a surfactant.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon		Republic of Korea	PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

BLEACHING CLEANER THAT FOAMS

BACKGROUND ART

5 The present invention relates to a cleaner that foams for cleaning piping systems such as sink drains. More particularly, it relates to binary peroxide cleaning systems.

 Various cleaners are known for unclogging drain pipes in sinks, bathtubs, and the like (e.g. clogs due to the build-up of hair, solidified grease, oils, and food
10 debris). Many of these are alkaline granular solids. See e.g. U.S. patents 3,968,048, 4,088,596, and 4,664,836. The disclosure of these patents, and of all other publications referred to herein, are incorporated by reference as if fully set forth herein.

 However, completely granular systems cannot be readily uniformly
15 distributed along the drain pipe. Also, they sometimes have slow reaction times, require the use of costly components and/or costly stabilizers, or require the use of a very high (and thus dangerous) pH levels.

 The art has also developed liquid drain cleaners. While such liquids have some advantages, they can be less effective than the granular drain cleaners in
20 removing certain types of clogs. Moreover, such liquids also often do not sufficiently clean vertical surfaces. This can lead to premature reclogging.

 Another problem with some drain cleaner formulations is that the ingredients may be unstable during storage such that premature reactions degrade later performance potential.

25 Thus, a need exists for an improved drain cleaner system.

DESCRIPTION OF INVENTION

30 In one aspect the invention provides a liquid cleaner having two parts, Parts A and B. The parts are kept physically separated until use. Part A contains a peroxide (e.g. hydrogen peroxide). Part B is a compound selected from the group consisting of a hypochlorite, a manganese containing material (e.g. a manganese salt), a carbonate, and a hypochlorite generator. At least one of Part A and Part B
35 is a liquid, and at least one of Part A and Part B also has a surfactant.

In one form Part A also has an organic acid such as one selected from glycolic acid, citric acid, lactic acid, boric acid, adipic acid, fumaric acid, malic acid, succinic acid, and tartaric acid. Other acids may also be used, but it is preferred to use relatively mild acids that keep hydrogen peroxide stable in storage without generating noxious smells.

The hypochlorite is preferably sodium hypochlorite, calcium hypochlorite or other alkali metal and alkaline earth metal hypochlorites. The surfactant is preferably an anionic or nonionic foaming surfactant. The carbonate is preferably an alkali metal carbonate, alkali metal bicarbonate, or alkaline earth metal carbonate. Water is preferably the majority of one of Part A and Part B.

A hypochlorite generator is a compound that generates a hypochlorite and is preferably an alkali metal dichloroisocyanurate. Other suitable hypochlorite generators are those described in U.S. patent 4,664,836.

Various bases (e.g. sodium hydroxide) can be added to Part B. In the alternative, an excess of sodium hypochlorite can be added so that the hypochlorite will cause the hydrogen peroxide to degenerate, with the excess acting as an additional active cleaner.

The invention has the advantage over completely solid systems of not requiring water from an outside source.

In yet another form the invention provides a method of removing an organic material from an interior surface of a piping system (e.g. a drain pipe). One mixes Part A and Part B to thereby create foam. One then exposes the organic material to the resulting foam. The foam helps the cleaning active(s) contact the organic material.

In yet another form, other peroxide generators (besides hydrogen peroxide) are substituted for hydrogen peroxide. Peroxide "generators" are compounds such as a perborate, a percarbonate, a peroxyurea compound, persilic acid and hydrogen peroxide adducts of pyrophosphates, citrates, sodium sulfate, and sodium silicate, which readily release a peroxide in aqueous solution.

Where the surfactant is in Part A, the surfactant should be stable in the presence of hydrogen peroxide. Preferably, the surfactant is between .01% and 10% of Part A, with .05% to 6% being especially preferred.

Foaming surfactants that may be employed in the present invention include anionic, nonionic and amphoteric surfactants, and mixtures thereof. Suitable

anionic surfactants include alpha olefin sulfonates, the alkyl aryl sulfonic acids and their alkali metal and alkaline earth metal salts such as sodium dodecyl benzene sulfonate, magnesium dodecyl benzene sulfonate, disodium dodecyl benzene disulfonate and the like, as well as the alkali metal salts of fatty alcohol esters of sulfuric and sulfonic acids, the alkali salts of alkyl aryl (sulfothioic acid) esters, alkyl thiosulfuric acid and soaps such as coco or tallow, etc.

Preferred anionics include sodium dodecyl benzene sulfonate available under the tradename Nacconal 40-G from Stepan Company, Northfield, Illinois, and sodium lauryl sulfate ("SLS") because of its foam enhancing properties, and to a lesser degree because of its detergency, wetting, and emulsifying properties. SLS is available in dry form under the trade designation Stephanol ME-Dry from the Stepan Chemical Company.

Suitable nonionic surfactants include the ethylene oxide esters of alkyl phenols such as (nonylphenoxy) polyoxyethylene ether, the ethylene oxide esters of fatty alcohols such as tridecyl alcohol polyoxyethylene ether, the propylene oxide ethers of fatty alcohols, the ethylene oxide ethers of alkyl mercaptans such as dodecyl mercaptan polyoxyethylene thioester, the ethylene oxide esters of acids such as the lauric ester of methoxy polyethylene glycol, the ethylene oxide ethers of fatty acid amides, the condensation products of ethylene oxide with partial fatty acid esters of sorbitol such as the lauric ester of sorbitan polyethylene glycol ether, and other similar materials.

Suitable amphoteric surfactants include the fatty imidazolines, such as 2-coco-1 hydroxyethyl-1 carboxymethyl-1hydroxylimidazoline and similar compounds made by reacting monocarboxylic fatty acids having chain lengths of 10 to 24 carbon atoms with 2-hydroxy ethyl ethylene diamine and with monohalo monocarboxylic fatty acids.

An additional class of suitable foaming surfactants are amine oxides which demonstrate cationic surfactant properties in acidic pH and nonionic surfactant properties in alkaline pH. Example amine oxides include alkyl dimethyl amine oxide, dihydroxyethyl cocamine oxide, tallowamidopropylamine oxide and lauramine oxide.

One mode of forming the foam is to have hypochlorite in (or from) Part B react with hydrogen peroxide in Part A to release oxygen in an alkaline environment, e.g.: $\text{NaOCl} + \text{H}_2\text{O}_2 \rightarrow \text{NaCl} + \text{O}_2 + \text{H}_2\text{O}$. The released oxygen causes the surfactant to foam, thereby providing very effective surface contact properties. An

excess of hypochlorite is preferred as it will act to dissolve hair, while also bleaching.

Alternatively, manganese containing material, such as a salt of manganese (e.g. manganese citrate derived via manganese sulfate and sodium citrate) can be included in Part B. If desired, a releasing compound (e.g. an alkali metal or alkaline earth metal halide such as calcium chloride) can be present in Part A. When the parts are mixed, the calcium readily displaces the manganese from the citrate complex, and the Mn^{++} reacts with H_2O_2 . Again, in this system, oxygen causes the foaming. However, the reaction time is slower than that when hypochlorite is used.

A third mode of operation uses a carbonate to release carbon dioxide when exposed to the acid from Part A. The hydrogen peroxide in this formulation acts as a bleach, with the foaming due to the carbon dioxide.

Alternatively, Part A can be sold as an additive for existing drain cleaners (e.g. a solid sodium perborate tablet to be used with a liquid drain cleaner containing sodium hypochlorite and surfactant).

The drain cleaner creates foam very rapidly when hydrogen peroxide itself is in Part A. Note that the problem of the instability of hydrogen peroxide during storage in an alkaline environment is overcome.

To avoid a possible problem caused by unintended metal contamination in Part A (and thus premature hydrogen peroxide degradation during storage), a stabilizer/chelating agent (such as Monsanto's Dequest, an aminophosphonate) can be added to Part A. Such chelating agents sequester metals.

If desired, enzymes and/or bacteria can also be added to the cleaner system. Suitable enzymes for use in the present invention include, for example, protease, amylase, cellulase, lipase and mixtures thereof. Preferably, the enzyme is a mixture of the above listed enzymes available under the tradename Otimase from Novo Nordisk Bioindustrials Inc., Danbury, Connecticut. Enzymes, in commercially available forms, are typically present in amounts from about 0.1% to about 50%, preferably from about 0.1% to about 10%, and most preferably from about 1% to about 5% by weight of the cleaner.

If bacteria is used as the drain opening active, it is typically present in a commercially available form in amounts from about 0.1% to about 50%, preferably from about 0.1% to about 20%, and most preferably from about 1% to about 10%

by weight of the cleaner. Suitable bacteria are those which are specially developed for waste and sewer treatment.

The objects of the present invention therefore include providing a cleaner of the above kind:

- 5 (a) having desirable declogging and bleaching characteristics;
- (b) having excellent cleaning capability with respect to organic materials commonly found in drains;
- (c) which is relatively inexpensive to produce;
- (d) which uses environmentally acceptable components;
- 10 (e) which is stable during storage; and
- (f) which delivers a cleaning active to a large area of the drain via foam.

These and still other objects and advantages of the present invention (e.g. methods for using such liquid cleaners) will be apparent from the description which follows.

The following description is merely of the preferred embodiments. Thus, the claims
15 should be looked to in order to understand the full scope of the invention.

MODES OF CARRYING OUT THE INVENTION

20 The following are examples of several "liquid" cleaners. By liquid cleaner, we mean that at least one of Part A or Part B is a liquid. Final pH's in the 6-10 range are preferred, with pH 8-9 being particularly preferred. "Non-caustic" compositions, with less than 5% excess NaOH or KOH, can be created. For Examples I-III a 1:1 mixture of Part A and Part B (by volume) can be made.

Example I

	<u>Range</u>	<u>Specific</u>
A) Hydrogen Peroxide	3.0-6.0%	3.0%
Organic Acid	0.0-0.5%	0.0%
Dequest	0.0-0.5%	0.0%
30 Surfactant	0.5-6.0%	1.5%
Water	remainder	remainder
B) Sodium Hypochlorite	6.0-12%	8.0%
Sodium Hydroxide	0.0-5%	0.0%
35 Water	remainder	remainder

Example II

		<u>Range</u>	<u>Specific</u>
5	A) Hydrogen Peroxide	.1-7.0%	6.0%
	Organic Acid	0.5-20%	12.0%
	Dequest	0.0-0.5%	0.0%
	Surfactant	0.5-6.0%	1.5%
	Water	remainder	remainder
10	B) Sodium Bicarbonate	1.0-12%	8.0%
	Sodium Hydroxide	0.1-2%	0.0%
	Water	remainder	remainder

Example III

		<u>Range</u>	<u>Specific</u>
15	A) Hydrogen Peroxide	3.0-7.0%	6.0%
	Organic Acid	0.0-0.5%	0.0%
	Dequest	0.0-0.5%	0.0%
	Surfactant	0.5-6.0%	1.5%
20	Calcium Chloride	0.0-1%	0.3%
	Water	remainder	remainder
25	B) Manganese Sulfate	0.1-1%	0.6%
	Sodium Hydroxide	0.0-1%	0.1%
	Sodium Citrate	0.2-5%	1.2%
	Water	remainder	remainder

Example IV

- 30 A) 10g sodium percarbonate
- B) 500g commercially available liquid drain cleaner
(3.45% NaOCl) (Drano7 Clog Remover)

Hair Dissolving Test

35 A cylinder was used to measure the invention's ability to dissolve hair (one of the most difficult clog components typically encountered). The Example IV 510 g was added to 150 ml of 100 degree Fahrenheit water along with 5 g of human hair clippings. The solution was then left overnight. The remaining hair was then strained out, rinsed, dried in an oven, and then weighed. This dissolved 3.4 g more

40 of the hair than a control without the cleaning solution.

Note that heat when the hypochlorite is in excess with respect to the hydrogen peroxide the foam will have good bleaching properties.

It should be appreciated that other forms of the invention are also possible. For example, as with other drain cleaners, a variety of conventional fragrances and colorants can be added.

Industrial Applicability

A liquid drain cleaner that foams can be prepared from the cleaners of the present invention.

CLAIMS

We claim:

1. A cleaner comprising Parts A and B which are physically separated until use, wherein:

5 Part A comprises a peroxide;

Part B is a compound selected from the group consisting of a hypochlorite, a manganese containing material, a carbonate, and a hypochlorite generator;

at least one of Part A and Part B is a liquid; and

at least one of Part A and Part B also contains a surfactant.

10

2. The cleaner of claim 1, wherein Part A also contains an acid, and Part B is an alkaline solution.

15

3. The cleaner of claim 2, wherein the acid is selected from the group consisting of glycolic acid, citric acid, lactic acid, boric acid, adipic acid, fumaric acid, malic acid, succinic acid, and tartaric acid.

20

4. The cleaner of claim 1, wherein the hypochlorite is selected from the group consisting of sodium hypochlorite, calcium hypochlorite and other alkali metal and alkaline earth metal hypochlorites.

5. The cleaner of claim 1, wherein the surfactant is selected from the group consisting of anionic and nonionic surfactants.

25

6. The cleaner of claim 1, wherein the carbonate is selected from the group consisting of alkali metal carbonate, alkali metal bicarbonate, and alkaline earth metal carbonate.

30

7. The cleaner of claim 1, wherein Part A and Part B each contain at least 50% water.

8. The cleaner of claim 1, wherein there is at least 5% hypochlorite in Part B and at least 2% hydrogen peroxide in Part A.

9. The cleaner of claim 1, further comprising a material selected from the group consisting of enzyme and bacteria.

10. A method of removing an organic material from an interior surface of a piping system, comprising:

mixing Part A and Part B of the claim 1 cleaner so as to create foam; and exposing the organic material to the resulting foam.

11. A cleaner comprising Parts A and B which are physically separated until use, wherein:

Part A comprises a peroxide generator;

Part B is a compound selected from the group of a hypochlorite, a manganese containing material, a carbonate, and a hypochlorite generator; at least one of Part A and Part B is a liquid; and at least one of Part A and Part B also contains a surfactant.

INTERNATIONAL SEARCH REPORT

National Application No
PCT/US 98/01744

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C11D3/39 C11D3/395 C11D3/20 C11D3/10 C11D17/04
C11D3/00 C11D11/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE WPI Section Ch, Week 8443 Derwent Publications Ltd., London, GB; Class D25, AN 84-267236 XP002068789 & JP 59 164 399 A (LION CORP) see abstract	1,4,5,7, 8,10,11
X	WO 95 16023 A (UNILEVER PLC ; UNILEVER NV (NL); SMITH GILLIAN (GB); SMITH ROYSTON) 15 June 1995 see page 5, line 27 - page 8, line 27 see page 11, line 30 - page 13, line 6 -/--	1-3,5,6, 11

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

19 June 1998

Date of mailing of the international search report

06/07/1998

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040. Tx. 31 651 epo nl.
Fax: (+31-70) 340-3016

Authorized officer

Richards, M

INTERNATIONAL SEARCH REPORT

national Application No

PCT/US 98/01744

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>DATABASE WPI Section Ch, Week 8611 Derwent Publications Ltd., London, GB; Class D25, AN 86-071395 XP002068790 & JP 60 013 897 A (LION CORP) see abstract</p>	1,4,7, 10,11
X	<p>DATABASE WPI Section Ch, Week 8515 Derwent Publications Ltd., London, GB; Class A97, AN 85-089699 XP002068791 & JP 60 038 497 A (LION CORP) see abstract</p>	1,6,7, 10,11
X	<p>DATABASE WPI Section Ch, Week 8351 Derwent Publications Ltd., London, GB; Class D25, AN 83-846899 XP002068792 & JP 58 191 800 A (KOYO KASEI KK) see abstract</p>	1,6,10, 11
P,X	<p>WO 97 31087 A (CLOROX CO) 28 August 1997 see example 1</p>	1,5,6,11
X	<p>DATABASE WPI Section Ch, Week 9513 Derwent Publications Ltd., London, GB; Class D25, AN 95-094103 XP002068793 & JP 07 018 298 A (HOSHI M) see abstract</p>	1,4,10
X	<p>DATABASE WPI Section Ch, Week 8412 Derwent Publications Ltd., London, GB; Class A97, AN 84-071115 XP002068794 & JP 59 024 798 A (LION CORP) see abstract</p>	1,10,11
X	<p>PATENT ABSTRACTS OF JAPAN vol. 096, no. 009, 30 September 1996 & JP 08 120299 A (LION CORP), 14 May 1996, see abstract</p>	1,11

INTERNATIONAL SEARCH REPORT

Information on patent family members

National Application No

PCT/US 98/01744

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 9516023	A	15-06-1995	AU 1240695 A	27-06-1995
			BR 9408256 A	10-12-1996
			CN 1141647 A	29-01-1997
			EP 0733097 A	25-09-1996
			HU 76860 A	29-12-1997
			JP 9506130 T	17-06-1997
<hr/>				
WO 9731087	A	28-08-1997	AU 1962997 A	10-09-1997
			EP 0827530 A	11-03-1998